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DOI:
10.1016/j.chemosphere.2017.02.096

Document Version
Peer reviewed version

Citation for published version (Harvard):
Al-Omran, LS & Harrad, S 2017, 'Influence of sampling approach on concentrations of legacy and "novel" brominated flame retardants in indoor dust', *Chemosphere*, vol. 178, pp. 51-58.
https://doi.org/10.1016/j.chemosphere.2017.02.096

INFLUENCE OF SAMPLING APPROACH ON CONCENTRATIONS OF LEGACY AND "NOVEL" BROMINATED FLAME RETARDANTS IN INDOOR DUST

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ABSTRACT

The study investigates the impact of sampling method on the concentrations of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) and NBFRs (PBEB, EH-TBB, BEH-TEBP, BTBPE and DBDPE) in indoor dust. A total of 36 dust samples were collected from 12 homes in Birmingham, UK (3 samples per home comprising researcher collected dust – both RCD from the living room (RCDL) and bedroom (RCDB), with an additional householder vacuum dust sample - HHVD). BDE-209 was the predominant compound, with average concentrations of 2642, 2336 and 2634 ng/g in RCDL, RCDB and HHVD respectively. The next most abundant BFR was BEH-TEBP, followed by DBDPE, with average concentrations of 306, 339 and 233 ng/g for BEH-TEBP and 155, 91 and 152 ng/g for DBDPE in RCDL, RCDB and HHVD respectively. Average concentrations of $\Sigma_6$tri-hexa-BDEs were 47, 41, and 24 ng/g in RCDL, RCDB and HHVD respectively. With the exception of $\Sigma_6$tri-hexa-BDEs, BDE-153, BDE-99 and to some extent BEH-TEBP, no significant differences were found between BFR concentrations in RCD and HHVD. Statistically significant correlations were observed between concentrations of $\Sigma_6$tri-hexa-BDEs, BEH-TEBP and DBDPE in HHVD and in both RCDL and RCDB. However, comparison of estimates of exposure via dust ingestion based on these two sampling methods revealed that using householder vacuum dust underestimates exposure, particularly for $\Sigma_6$tri-hexa-BDEs, and to some extent for BEH-TEBP. In contrast, HHVD could be a viable alternative to RCD as a metric of exposure for higher brominated BFRs.

HIGHLIGHTS

- BFRs measured in researcher-collected (RCD) and house holder vacuum dust (HHVD).
- Concentrations of more volatile BFRs and BEH-TEBP in HHVD lower than those in RCD.
- Concentrations of less volatile do not vary significantly between the two sampling methods.
- $\Sigma_6$tri-hexa-BDEs, BEH-TEBP and DBDPE in HHVD and RCD significantly correlated.
- Using HHVD may underestimate exposure for $\Sigma_6$tri-hexa-BDEs and BEH-TEBP.

1. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) and "novel" brominated flame retardants (NBFRs) are chemicals added to a wide range of consumer products (electrical and electronic equipment, textiles, polyurethane and polystyrene foams) to meet flame retardancy standards set by various jurisdictions worldwide (Danish EPA, 2013; USEPA, 2014). Since in most applications these chemicals are used additively, they can transfer from such products into the environment (WHO, 1997; Alaee et al., 2003; USEPA, 2010). Evidence of their persistence and capacity for bioaccumulation, coupled with their adverse health effects have led to concern about human exposure (USEPA, 2006; 2008a; 2008b; 2008c; NICNAS, 2007; Noyes et al., 2010; Chevrier et al., 2010; EFSA, 2012; European Commission, 2012; Johnson et al., 2013; Li et al., 2014; Mankidy et al., 2014; Mariani, et al., 2015). Ingestion of indoor settled dust appears to represent a major pathway of exposure to BFRs particularly for young children (Jones-Otazo et al., 2005; Wilford et al., 2005; Harrad et al., 2008a: 2008b; 2010; Abdallah et al. 2008; Lorber, 2008; Roosens et al., 2009; Wang et al., 2010; Besis and Samara 2012; Stapleton et al., 2012; Qi et al., 2014; Hoffman et al., 2015).

To date, there are few studies that have investigated the association between indoor dust sampling method and the concentration of pollutants. For determining exposure of children to lead-contaminated household dust, early studies investigated different house dust sampling methods, indicating that the HVS3 (high-volume small surface sampler) had the highest level of precision among different standardised vacuuming and wipe sampling methods (Sterling et al., 1999), due to the small particles that can be retained by the HVS3 (Lioy et al., 2002). This method has subsequently been widely used, although it can be expensive, complicated and time-consuming (Mercier et al., 2011; USEPA, 2008d). Thus, commercial household vacuum cleaners are widely used as an alternative to the HVS3. By using a household vacuum cleaner, two approaches for dust collection are commonly used in studies of indoor contaminants. One of these approaches involves householders providing the contents of their vacuum cleaners to the researchers (Harrad et al., 2006; Suzuki et al., 2006; Kopp et al., 2012; Shen et al., 2015; Cristale et al., 2016). The principal advantages of the householder vacuum cleaner approach are that: it reflects indoor contamination from all rooms, is cost-effective, provides a large quantity of dust in a short time, and enhances donor compliance, by obviating the need for researchers to enter the home (Harrad et al., 2010). However, dust collected by this approach may be contaminated by the inner part of the vacuum cleaner, thereby reducing the accuracy of this method. Moreover, spatial variability, temporal variability and dust loading cannot be

assessed by this method, as the time and locations covered by the sample are unknown. In addition, vacuum cleaner sampling rates are variable (Harrad et al., 2010). Another approach involves the use of a commercial vacuum cleaner by the researchers themselves by using standardized procedures and specific accessories such as socks inserted in the sampling train to retain dust (Brommer et al., 2012; Ali et al., 2013; Harrad et al., 2016), Soxhlet thimbles (Allen et al., 2008; Stapleton et al., 2012) and filters (Björklund et al., 2012; Thuresson et al., 2012; Newton et al., 2015). The main advantages of such researcher-collected dust approaches are that: it minimises contamination of the sample due to specific accessories which are replaced or cleaned between taking each sample, and that it provides information about the specific time and location of collection of each dust sample, thereby facilitating study of within-room and within-home spatial and temporal variations in BFR concentrations. However, in comparison with the householder vacuum approach, this method is expensive and time-consuming, and may possibly hinder donor compliance as it requires entry of the researcher to the sampled microenvironment (Harrad et al., 2010). Only two studies (Allen et al., 2008; Björklund et al., 2012) have investigated the variation between researcher-collected and household vacuum approaches for analysing PBDE in indoor dust. Overall, the two studies reported PBDE concentrations in researcher-collected dust exceeded significantly those in householder-donated vacuum cleaner dust.

The aim of this study is to investigate the impact of two commonly-employed dust sampling methods on the concentrations of eight PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and five NBFRs: pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE) in indoor dust and to evaluate the extent to which these sampling methods influence exposure assessments to BFRs via dust ingestion. To our knowledge, this study is the first investigation of the influence of sampling approach on concentrations of NBFRs in indoor dust.

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

Dust samples (n = 36) were collected from 12 homes between September 2014 and April 2015. In each home, two floor dust samples were collected by the researcher (researcher-collected dust- RCD) with the householder additionally providing the contents of their vacuum cleaner

(household vacuum dust- HHVD). RCD samples were obtained from the living room (RCDL) and bedroom (RCDB) of each house according to a clearly defined standard protocol (Harrad et al., 2008a). Briefly, by using a handheld vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), 1 m^2 of carpeted floor area was vacuumed for 2 min, using 25 μm pore size nylon sample socks mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in plastic bags. Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using isopropanol-impregnated disposable wipes and dried between collections. HHVD samples were collected at the same time. The dust bag from the householder's own vacuum cleaner was wrapped in aluminium foil and sealed in a plastic bag. All samples were stored at −20 ˚C until analysis. Prior to analysis, dust samples were passed through a pre-cleaned, *n*-hexane rinsed 250 μm mesh steel sieve covered with the lid and shaken for 3-5 min. Field blanks were conducted which consisted of sodium sulfate that spread on aluminium foil, collected using the vacuum cleaner used to collect RCD and treated as a sample.

2.2. Sample extraction, clean up and instrumental analysis

PBDEs and NBFRs in dust samples were analysed following the same extraction method as reported elsewhere (Ali et al., 2011; Van den Eede et al., 2012, Al-Omran and Harrad 2016a; 2016b) with minor modifications. Accurately weighted aliquots of dust (~ 0.1 g) were spiked with a mixture of internal standards (20 ng of BDE-77, BDE-128, ^{13}CBTBPE, ^{13}CBEH-TEBP, and 40 ng of ^{13}CBDE-209) in isooctane. Dust samples were extracted with 2 mL *n*-hexane: acetone (3:1 v/v), 2× (vortexed for 2 min, sonicated for 5 min) and centrifuged at 3500 rev/min for 5 min. The extraction process was repeated three times and the combined extracts were evaporated to incipient dryness under a gentle nitrogen stream, resolubilised in 1 mL of *n*-hexane.

Concentrated crude sample extracts were purified according to a previously reported method (Al-Omran and Harrad 2016a; 2016b) involving two steps. Briefly, in the first step, the extract was fractionated into two fractions (F1 and F2) using a 2 g Florisil SPE cartridge. F1 (containing PBDEs, DBDPE and PBEB) was eluted with 12 mL of hexane and F2 (containing the rest of the targeted NBFRs) was eluted with 15 mL ethyl acetate. After evaporation to 1 mL, a second purification step for F1 was conducted on 2 g acid silica (44% w/w) eluted with

15 mL *n*-hexane/DCM (1:1, v/v). F2 was evaporated to dryness, resolubilised in 3-5 mL of hexane, then evaporated to 1 mL, and eluted with 12 mL *n*-hexane/DCM (1:1, v/v) using an aminopropyl functionalised silica column (0.5 g). F1 and F2 were combined and evaporated to incipient dryness, before resolubilisation in 100 µL of iso-octane containing PCB-129 at 250 pg/µL ready for GC/MS analysis.

Target PBDEs and NBFRs were quantified using a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both (Thermo Fisher Scientific, USA) according to our previous study of BFRs in indoor dust (Al-Omran and Harrad 2016b). The GC was equipped with a programmable temperature vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter, 0.25 µm film thickness). The MS was operated in the electron capture negative ion (ECNI) mode. Table S1 shows quantification ions, qualification ions and retention times monitored for target compounds, internal standards (IS) and the recovery determination standard (RDS).

2.3. Quality assurance/Quality control

All glassware was cleaned by soaking them overnight in a detergent solution. After washing, glassware and Pasteur pipettes were heated to 470 ˚C for 5 h. Before use, glassware was rinsed with acetone and hexane. To avoid any degradation that may occur via exposure to light, glassware and the Turbovap instrument were covered with aluminium foil. To assess any possible contamination during sample preparation and analysis method, one laboratory blank was processed in parallel with every set of 6 dust samples and one quality control sample (NIST SRM 2585, organics in indoor dust) was processed with every 12 real dust samples. Limits of detection (LOD) were estimated based on a signal to noise ratio 3:1 and limits of quantification (LOQ) were estimated based on signal to noise ratio 10:1. Where a target compound (as was the case in some instances for BEH-TEBP and BDE-209) was detected a blank, the LOQ for that analyte was calculated as the mean plus 3 times the standard deviation of the concentrations detected in 10 blank samples. Field blanks (n = 5) were also collected to assess any contamination contributed as a result of sampling, transport and storage of samples, in addition to any introduced as a result of extraction and clean-up. The average of internal standard recoveries in dust samples ranged from 75-93%. PBDE and NBFR concentrations in SRM2585

detected in this study were in good agreement with the certified values and those reported in other studies. Tables S3, S4 and S5 report internal standard recovery values, along with PBDE and NBFR concentrations in SRM2585 detected in this study.

2.4. Statistical analysis

Statistical analysis of our data was performed using Microsoft Excel 2013 and IBM SPSS statistics software (V. 20). To test any differences in mean BFR dust concentrations between the two collection methods (researcher-collected and household vacuum), and between the two researcher-collected rooms (living room and bedroom) one way repeated measures ANOVA was performed. After testing for normality using the Shapiro–Wilk test confirmed our data to display a skewed distribution, data were transformed using the natural logarithm of concentrations (ng/g dw). For the purposes of statistical evaluation, all concentrations below LOQ were assigned a value of 0.5 LOQ. A p value < 0.05 was taken to indicate statistical significance. A Pearson correlation was used to test the relationship between BFR concentrations in dust collected via the two sampling methods.

3. RESULTS AND DISCUSSION

3.1. Influence of dust sampling approach on BFR concentrations

3.1.1 Detection frequencies and the relationship between BFRs

In all dust samples (n = 36), the detection frequency of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) ranged from 50% to 100%. The detection frequencies of BDE-209, BEH-TEBP and DBDPE were 100% in both researcher-collected dust (RCD) and household vacuum dust (HHVD). BDE-28, BDE-100, BDE-154, and PBEB were in the lowest detection frequencies. They were thus not accounted for individual statistical comparison, but were instead included in $\Sigma_7$tri-hexa-BDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) and Σ_5NBFRs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE). Table S6 lists detection frequencies of PBDEs and NBFRs in this study.

Among our target BFRs, BDE-209 was predominant, with average percentage contributions to ΣBFRs (sum of $\Sigma_7$tri-hepta-BDEs, BDE-209 and Σ_5NBFRs) of 83.2%, 82.7% and 85.9% in RCDL, RCDB and HHVD respectively. Σ_5NBFRs were the next most abundant parameter,

with average contributions of 15.1%, 15.8% and 13% in RCDL, RCDB and HHVD respectively. $\Sigma_7$tri-hepta-BDEs displayed the lowest average percentage contributions of our target BFRs. The average percentage contributions of BDE-99, BDE-47 and BDE-183 to $\Sigma_7$tri-hepta-BDEs were 44%, 45% and 38% for BDE-99, 29%, 27% and 23% for BDE-47, and 11%, 5.4% and 23% for BDE-183 in RCDL, RCDB and HHVD respectively. Of our target NBFRs, BEH-TEBP predominated, making mean percentage contributions to Σ_5NBFRs of 64%, 76% and 58%, followed by DBDPE which contributed 32%, 20% and 38% of Σ_5NBFRs in RCDL, RCDB and HHVD respectively. Figure 1 depicts the average percentage contributions and congener/compound profiles of target BFRs, tri-hepta-BDEs and NBFRs in RCDL, RCDB and HHVD.

3.1.2. Concentrations of PBDEs and NBFRs in indoor dust obtained via two different sampling methods

The three main commercial PBDE formulations (Penta-BDE, Octa-BDE and Deca-BDE) are represented in this study by $\Sigma_6$tri-hexa-BDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) as an indicator of Penta-BDE, BDE-183 as an indicator of Octa-BDE and BDE-209 as an indicator of Deca-BDE. In all dust samples, the highest concentrations of total target ΣPBDEs and Σ_5NBFRs were found in researcher-collected dust samples from living rooms (RCDL), with values of 4321 and 1450 ng/g for ΣPBDEs and Σ_5NBFRs respectively. BDE-209 was present at average concentrations of 2642, 2336 and 2634 ng/g, while those of BEH-TEBP were 309, 339 and 233 ng/g in RCDL, RCDB and HHVD respectively. Average concentrations of DBDPE were comparable in both RCDL and HHVD samples, with values of 155 and 152 respectively, while in RCDB it was 91 ng/g. $\Sigma_6$tri-hexa-BDEs average concentrations were 47.3 and 41.3 and 24.4 ng/g in RCDL, RCDB and HHVD respectively. For the rest of our target NBFRs, BTBPE was found in comparable average concentrations in RCDL and HHVD, with values of 11.0 and 11.2 respectively, while in RCDB, it was 9.5 ng/g. Average concentrations of EH-TBB in RCDL and RCDB were comparable (6.9 and 6.4 ng/g) exceeding those in HHVD samples (4.9 ng/g). Tables 1 and 2 provide statistical summaries of concentrations of PBDEs and NBFRs in RCDL, RCDB, and HHVD samples.

Comparison with previous studies (Harrad et al., 2008a; 2008b) in Birmingham, UK, revealed median concentrations of PBDEs in this study to be lower than in the earlier studies by a factor of 2.7 for Σ_8PBDEs, while DBDPE increased by a factor of 3.6. While our study is based on

too few homes to provide a definitive temporal trend; these data are not inconsistent with restrictions on PBDE use and possible concomitant increased use of NBFR alternatives.

3.1.3. Comparison of BFR concentrations in dust samples from two sampling methods

Tables 1 and 2 show concentrations of BDE-47, BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and EH-TBB in researcher-collected dust from both living room (RCDL) and bedroom (RCDB) exceed those in household vacuum dust (HHVD). In contrast, BDE-183 in HHVD was higher than in RCDL and RCDB. Moreover, BDE-209, BTBPE, and DBDPE concentrations in HHVD were only higher than in RCDB and were comparable in both RCDL and HHVD. Table S7 lists the average concentration ratios for RCDL/ HHVD and RCDB/ HHVD for BDE-47, BDE-99, BDE-153, BDE-BDE-183, BDE-209, EH-TBB, BEH-TEBP and DBDPE.

One way repeated measures ANOVA tests were applied to compare means of BFR concentrations in RCDL, RCDB and HHVD. This revealed that, with the exception of $\Sigma_6$tri-hexa-BDEs, BDE-153, BDE-99 and to a moderate extent BEH-TEBP, these differences were not statistically significant ($p > 0.05$). Concentrations of $\Sigma_6$tri-hexa-BDEs and BDE-153 in researcher-collected dust (RCDL and RCDB combined) exceeded significantly those in the household vacuum dust with p values of 0.012 and 0.038 for $\Sigma_6$tri-hexa-BDEs, and 0.025 and 0.016 for BDE-153 in RCDL and RCDB respectively. BDE-99 concentrations in RCDL exceeded significantly those in HHVD with a p value of 0.015. Moreover, BEH-TEBP concentrations in RCDL exceeded those in HHVD at a moderate level of significance (p = 0.077). ANOVA tests revealed, with the exception of BDE-183, no significant differences ($p > 0.05$) in BFR concentrations between the living room and bedroom. With respect to BDE-183, concentrations in the living room exceeded significantly those in the bedroom (p = 0.001). Based on our results, Penta-BDE and to a lesser extent BEH-TEBP displayed important differences between the two sampling methods, while concentrations of Deca-BDE, Octa-BDE, EH-TBB, BTBPE and DBDPE did not appear significantly impacted by the sampling method employed.

To our knowledge, only two studies (Allen et al., 2008; Björklund et al., 2012) have compared PBDE and HBCDD concentrations in house dust collected via different sampling methods. In a comprehensive study of indoor dust from 20 homes in Boston, USA; Allen et al., (2008) compared concentrations of PBDEs in dust collected using household vacuum cleaner and

297 researcher-collected (from living room and bedroom) methods. The study reported that Penta-
298 BDE (ΣBDE-17, 28/33, 47, 49, 66, 75, 85/155, 99, 100, 183, 153 and 154) concentrations in
299 researcher-collected dust samples exceeded significantly those in the household vacuum dust
300 for both living rooms (p = 0.001) and bedrooms (p = 0.002). In addition, the concentrations of
301 Deca-BDE formulation congeners (BDE-206, 207, 208 and 209) in the researcher-collected
302 dust from the living room exceeded significantly (p = 0.02) those in the household vacuum
303 dust, with such significant differences to the household vacuum dust not observed for bedroom
304 researcher-collected samples. Moreover, the same study found no significant difference
305 between Octa-BDE concentrations in dust obtained via the two sampling methods. With the
306 exception of the concentrations of Deca-BDE formulation congeners in researcher-collected
307 dust from the living room, our outcomes are consistent with the study of Allen et al. (2008),
308 despite the differences in PBDE distribution profiles between the UK and USA, different
309 sampling accessories (nylon sock and cellulose extraction thimble), different vacuum cleaner
310 brands and different dust particle size fractions (< 500 μm and < 250 μm).
311
312 Based on dust samples from 19 Swedish homes, Björklund et al., 2012, investigated the
313 differences between PBDE and HBCDD concentrations in samples collected via researcher-
314 collected and household vacuum methods. The researcher-collected method employed
315 involved collection of settled house dust from elevated surfaces (1 m above the floor).
316 Concentrations of all targeted PBDE congeners (BDE-28, BDE-47, BDE-49, BDE-66, BDE-
317 85, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-197, BDE-203, BDE-206, BDE-
318 207, BDE-208, and BDE-209) detected in researcher-collected dust exceeded significantly (P
319 < 0.001- 0.003) those collected using the household vacuum method. The significant
320 differences observed by Björklund et al. (2012) between researcher-collected method and
321 household vacuum method dust, exceeded those observed both in our study and that of Allen
322 et al. (2008). This implies that, in addition to the different sampling methods, sampling of
323 different surfaces (floor dust and elevated surface dust) exert an important influence on the
324 findings of the Swedish study. This is consistent with findings reported in our previous studies
325 (Al-Omran and Harrad 2016a; 2016b), that BFR concentrations in elevated surface dust
326 samples exceed significantly those in floor dust.
327
328 **3.1.4. Correlation between dust sampling methods**

329 Pearson correlation analysis was performed on log-transformed data to determine the
330 relationship between BFR concentrations in household vacuum dust (HHVD) and researcher-
331 collected dust (RCD) from the living room (RCDL) and bedroom (RCDB). The strongest
332 correlations observed between HHVD and RCD methods were for BEH-TEBP concentrations
333 in the living room (R = 0.793, p = 0.002) and bedroom (R = 0.883, p = < 0.001). Likewise,
334 concentrations of $\Sigma_6$tri-hexa-BDEs in HHVD correlated with those in RCDL (R = 0.583, p =
335 0.047) and RCDB (R = 0.588, p = 0.044), as well as those of DBDPE for which the
336 corresponding correlations with HHVD concentrations were (R= 0.643, p = 0.024) and (R =
337 0.634, p = 0.027) for RCDL and RCDB respectively. Moreover, HHVD concentrations were
338 moderately (R = 0.532, p = 0.075) associated with RCDL concentrations for BDE-209, and
339 with RCDB for EH-TBB (R = 0.557, p = 0.060). Figure 2 shows scatter plots and Pearson
340 correlation coefficients obtained when plotting log-transformed concentrations of $\Sigma_6$tri-hexa-
341 BDEs, BEH-TEBP and DBDPE in household vacuum dust against concentrations in both
342 RCDL and RCDB. Table S8 shows Pearson correlation results describing the relationship
343 between BFR concentrations in dust samples collected by a researcher (RCDL and RCDB)
344 and household vacuum (HHVD) approaches.

345

346 In general, our findings reveal that BFR concentrations in dust collected via the two sampling
347 methods were highly correlated for BEH-TEBP, DBDPE, $\Sigma_6$tri-hexa-BDEs, and BDE-99, and
348 moderately correlated for BDE-209 and EH-TBB. In contrast, concentrations of BDE-47,
349 BDE-153, BDE-183, and BTBPE were not significantly correlated between researcher-
350 collected and household vacuum dust. For PBDEs, with the exception of BDE-209, these
351 findings are consistent with previous studies (Allen et. al 2008; Björklund et al., 2012).
352 However, Björklund et al., concluded that, when a single high value of BDE-209 was removed
353 from their data analysis, the correlation they observed between concentrations obtained via the
354 2 dust collection methods was no longer significant (Björklund et al., 2012).

355

356 **3.1.5 The impact of sampling approach on human exposure assessments to BFRs**

357 To evaluate the extent to which human exposure to our target contaminants via dust ingestion
358 is affected by the choice of sampling approach, we compared the median concentration (for
359 typical exposure) and 95th percentile (for high end exposure) in dust samples collected via the
360 two sampling approaches; researcher collected from the living room and bedroom and
361 household vacuum contents. This comparison revealed that the impact of sampling method on

estimates of exposure to BDE-99 and Σtri-hexa-BDEs was more important than for other target compounds. Concentrations of (and thus exposure to) BDE-99 and Σtri-hexa-BDEs in RCD exceeded substantially those in HHVD by factors of 1.5 and 3.5 for BDE-99 and 1.8 and 2.7 for Σtri-hexa-BDEs for the median and 95th percentile respectively. In addition, concentrations of BEH-TEBP based on analysis of RCD exceeded those for HHVD by factors of 1.4 and 1.5 for the median and 95th percentile respectively. This implies that exposure assessments for these compounds based on analysis of HHVD may be underestimates, particularly when making high-end exposure assessments. In contrast, concentrations of DBDPE in HHVD exceeded those in RCDB by factors of 1.1 and 2.3 for median and 95th percentile concentrations respectively, which implies that analysing HHVD may overestimate exposure to DBDPE. Table 3 illustrates RCDL/HHVD and RCDB/HHVD median and 95th percentile concentration ratios for BDE-99, $\Sigma_6$tri-hexa-BDEs, BDE-209, BEH-TEBP and DBDPE, which illustrate the impact of sampling method on typical and high-end exposure assessments.

4. CONCLUSIONS

This study found that concentrations of BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and – to some extent - BEH-TEBP were significantly lower in HHVD (household vacuum dust) than those in RCD (researcher-collected dust) from both living rooms and bedrooms. This might be due to volatilisation of BFRs as a result of the long residence times of dust in the household vacuum. In addition, RCD samples were collected from bedrooms and living rooms where large quantities of Penta-BDE and BEH-TEBP may have been used (in articles such as beds, chairs, and sofas), whereas the household vacuum cleaner would contain a complex integral of dust from the entire house, which would include rooms containing fewer products containing Penta-BDE, such as kitchens (Kuang et al., 2016) and hallways. Moreover, small particles (which we have shown previously to contain higher concentrations of some BFRs – Al-Omran and Harrad, 2016b) may have been lost through collecting and transferring processes from the vacuum bag. Our findings indicate that exposure assessments using HHVD may be underestimated for $\Sigma_6$tri-hexa-BDEs and BEH-TEBP, which suggest that this approach is a less suitable method for assessing human exposure to these compounds. However, it could be a viable alternative to RCD for higher brominated BFRs such as BDE-209.

Due to the different particle size distribution pattern of BFRs in indoor dust (Wei et al. 2009; Cao et al., 2013, 2014, 2015; Kefeni et al., 2014), future studies are recommended using particle size analyser to examine the particle size distribution pattern of BFR concentrations in obtained via

the two sampling methods, to test the hypothesis that a greater proportion of fine particles in RCD account for the higher BFR concentrations observed in such dust compared to HHVD. This is because the same compounds (BDE-99, BDE-153, $\Sigma_6$tri-hexa-BDEs and BEH-TEBP) that were significantly elevated in researcher collected compared to household vacuum collected dust, are also significantly higher in the finest particle size fractions of indoor dust (Al-Omran and Harrad, 2016b).

ACKNOWLEDGEMENTS

The authors express their thanks to all the dust donors from Birmingham, UK. Layla Salih Al-Omran acknowledges gratefully the Iraqi government for a PhD Scholarship, the Iraqi Establishment of Martyrs for financial support and the Ministry of Higher Education and Scientific Research for administrative support.

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Figure 1: Average percentage contributions and congener/compound profiles of target BFRs, tri-hepta-BDEs and NBFRs in RCDL, RCDB (researcher-collected dust from the living room and bedroom) and HHVD (household vacuum dust)

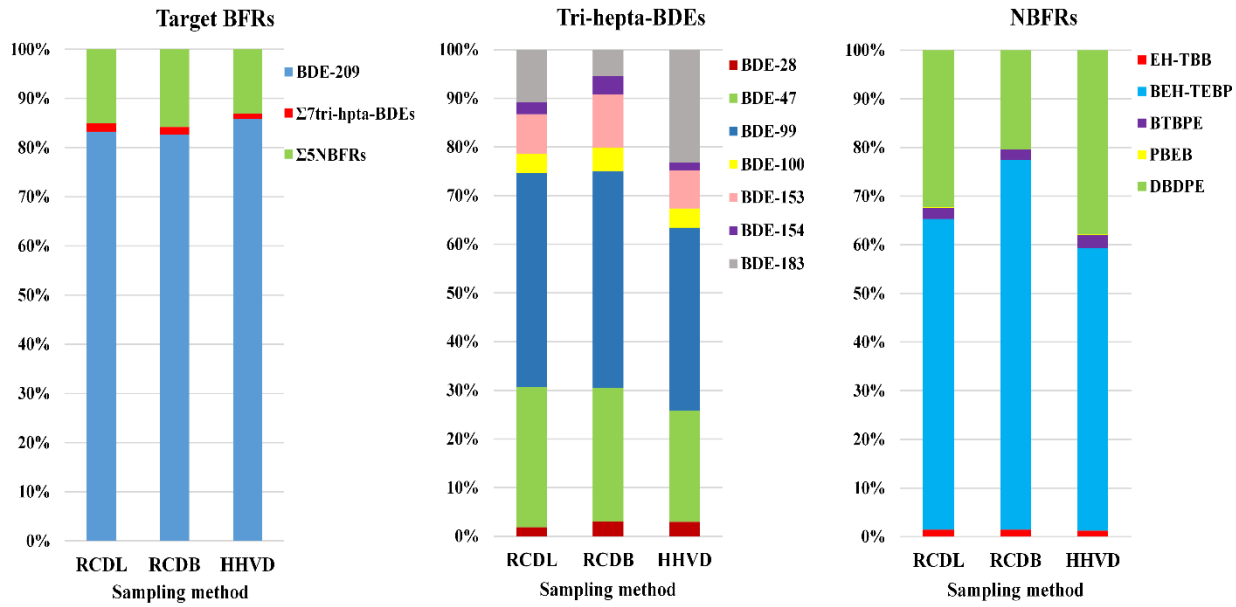

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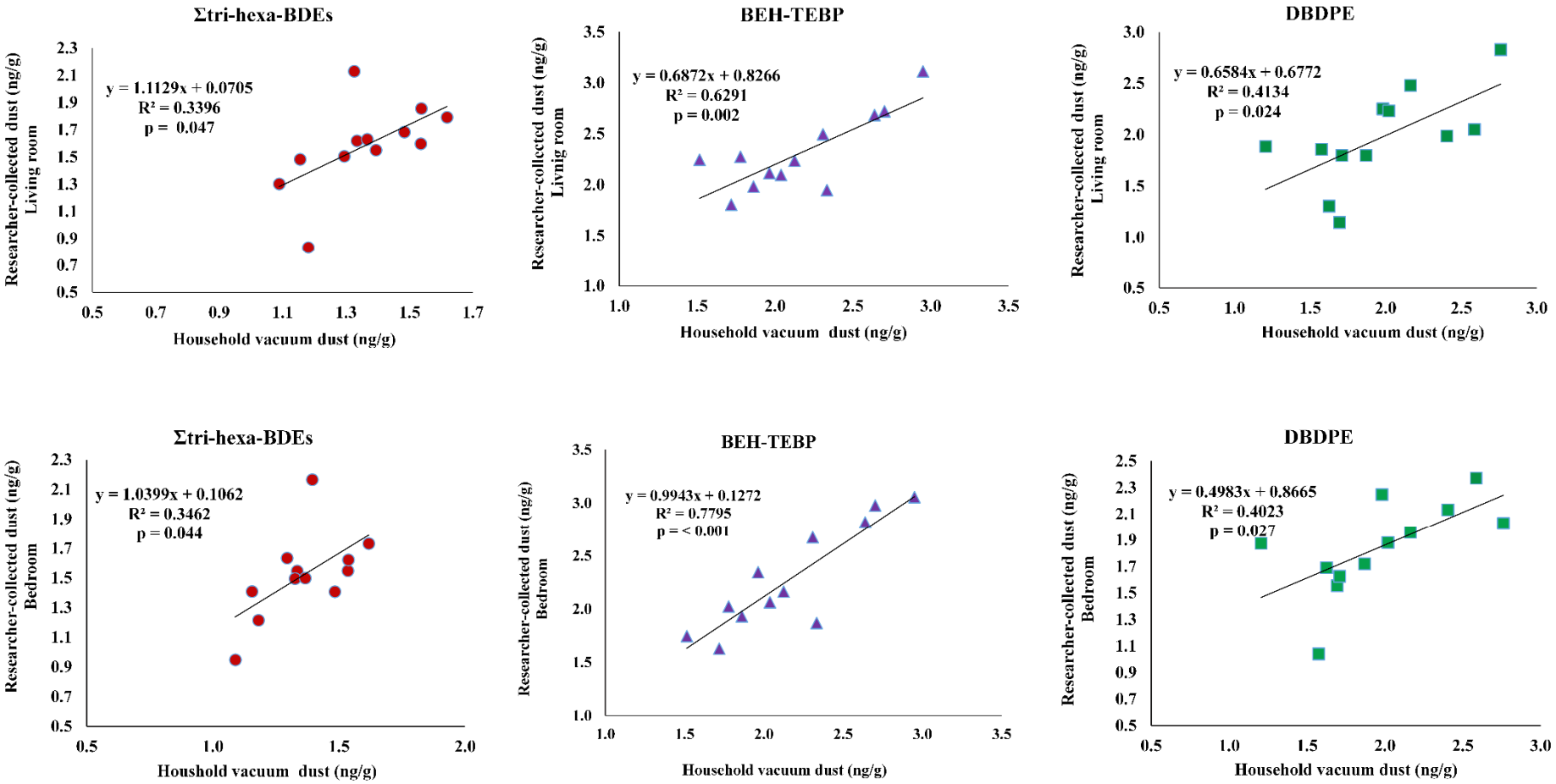
Figure 2: Correlations between log-transformed concentrations of $\Sigma_6$tri-hexa-BDEs, BEH-TEBP and DBDPE in household vacuum dust and researcher-collected dust from the living room and bedroom



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625 **Table 1: Summary statistics for PBDE concentrations (ng/g) in RCDL, RCDB**
626 **(researcher collected dust from the living room bedroom) and dust HHVD (household**
627 **vacuum dust)**

Target compound	Sampling method	Average	Median	Minimum	Maximum	Standard deviation
BDE-47	RCDL	15.3	13.0	< 0.1	44.8	11.9
	RCDB	12.0	11.1	< 0.1	31.9	7.8
	HHVD	7.4	6.8	< 0.1	14.3	5.1
BDE-99	RCDL	23.3	17.9	4.2	77.1	18.7
	RCDB	19.5	14.5	< 0.2	88.6	22.7
	HHVD	11.8	12.0	7.7	16.1	2.6
BDE-153	RCDL	4.3	4.1	< 0.2	7.3	1.8
	RCDB	4.8	4.0	1.4	14.7	3.6
	HHVD	2.5	2.9	< 0.2	5.9	2.1
$\Sigma_6$tri-hexa-BDEs	RCDL	47.3	40.7	6.8	135	32.6
	RCDB	41.4	33.5	8.9	147	35.4
	HHVD	24.4	22.4	12.3	41.5	9.1
BDE-183	RCDL	5.7	6.0	< 0.2	11.3	3.4
	RCDB	2.4	2.8	< 0.2	5.1	1.7
	HHVD	7.2	2.5	< 0.2	61.2	17.1
BDE-209	RCDL	2642	3066	466	4184	1354
	RCDB	2336	2232	1175	3944	780
	HHVD	2634	2462	1534	3779	802
Σ_8PBDEs	RCDL	2695	3112	474	4321	1363
	RCDB	2380	2272	1233	3985	775
	HHVD	2666	2519	1568	3795	797

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632 **Table 2: Summary statistics for NBFR concentrations (ng/g) in RCDL, RCDB**
633 **(researcher collected dust from the living room bedroom) and dust HHVD (household**
634 **vacuum dust)**

Target compound	Sampling method	Average	Median	Minimum	Maximum	Standard deviation
EH-TBB	RCDL	6.9	6.4	< 0.5	21.2	6.0
	RCDB	6.4	3.1	< 0.5	24.2	7.9
	HHVD	4.9	3.9	< 0.5	13.5	4.9
BTBPE	RCDL	11.0	11.2	< 2.8	21.4	7.4
	RCDB	9.5	9.8	< 2.8	15.8	4.9
	HHVD	11.2	8.0	< 2.8	35.7	11.5
BEH-TEBP	RCDL	306	175	64	1299	348
	RCDB	339	131	43	1139	380
	HHVD	233	121	33	890	256
DBDPE	RCDL	155	87	14	679	184
	RCDB	91	76	11	236	65
	HHVD	152	85	16	575	170
Σ_5NBFRs	RCDL	479	394	127	1450	382
	RCDB	446	225	104	1412	420
	HHVD	402	272	129	1302	345

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645 **Table 3: Median and 95th percentile concentration ratios of BDE-99, $\Sigma_6$tri-hexa-BDEs,**
646 **BDE-209 and DBDPE between researcher collected-dust from the living room and**
647 **bedroom (RCDL and RCDB) and household vacuum dust**

Compound	Sampling approach	Median	95th percentile
BDE-99	RCDL/HHVD	1.5	3.5
	RCDB/HHVD	1.2	3.4
$\Sigma_6$tri-hexa-BDEs	RCDL/HHVD	1.8	2.7
	RCDB/HHVD	1.5	2.6
BDE-209	RCDL/HHVD	1.2	1.1
	RCDB/HHVD	0.9	1.0
BEH-TEBP	RCDL/HHVD	1.4	1.3
	RCDB/HHVD	1.1	1.5
DBDPE	RCDL/HHVD	1.0	1.0
	RCDB/HHVD	0.9	0.4

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